Name: _____KEY_____

Chemistry 122-04 -- General Chemistry II **Spring 2006**

Test #1

Organic molecules, molecular structure and bonding theory, solubility, *(breathe now)*
phase transitions, spectroscopy, and kinetics

1. ***The basics.*** Please answer each of the following questions as tersely as possible. Explanations are only required where explicitly requested. (2 points each unless otherwise noted)

a) Please **draw the structural formula of an organic molecule that bears an oxygen-containing functional group**. Please **indicate the name of the functional group** that appears in the structure you have just drawn.

any alcohol, ether, ester, or carboxylic acid will do.
For example, CH_3OH, methanol, is an alcohol.

b) **Indicate the molecular (bond) geometry around a carbon atom that is attached to an oxygen atom** in the structure you have just drawn. If there are multiple carbons attached to oxygens in your structure, please pick one and indicate it with an arrow. (If you can't think of the appropriate term to describe this geometry, you may describe it in words.)

for methanol, the bond geometry around the carbon is tetrahedral

c) Please tell me **how many π bonds and how many σ bonds** are present in your structure.

methanol has five σ bonds and no π bonds

d) Indicate the kind of **orbital hybridization** you'd expect to find for the valence electrons of the carbon you chose for part (b).

for methanol, the orbital hybridization around the carbon is sp^3

e) Please tell me the **formal charge and oxidation number** of the carbon you chose for part (b).

for the carbon in methanol,
the formal charge is 4 - 4 = 0
the oxidation number is 4 - 6 = -2 (if real electronegativities are used)
[or 4-3 = +1 (if C and H are treated as equally electronegative)]

f) (1 pt each question) Consider the following phase change: $CH_3CH_2CH_3$ (l) --> $CH_3CH_2CH_3$ (g)

Will the molecules in the liquid phase or the gas phase be **interacting more closely**? liquid
Will the molecules in the liquid phase or the gas phase **have higher entropy**? gas
Will the phase transition, as written above, **consume energy or release energy**? consume

g) (1 pt each pair) Imagine a bond between each of the following pairs of atoms. For each pair,

- if you think that the bond will be a nonpolar covalent bond, please mark an "X" through the pair
- if you think that the bond will be a polar covalent bond, please circle the atom that will be more negatively charged
- if you think that the bond will be an ionic bond, please put a box around the atom that will form a cation

C and N S and N H and F

h) What **two characteristics** must a **molecule** posses in order to be polar?

It must have at least one polar bond, and it must be asymmetrical.

i) According to Molecular Orbital theory, what is the **fundamental difference in electron density** between a bonding MO and an antibonding MO? (That is to say, where are the electrons concentrated in each case?)

Bonding MOs have high electron density in the region between the nuclei of the atoms, thus bonding them together; Antibonding MOs have nodes -- zero electron density -- between nuclei, thus contributing nothing to the association of the atoms.

j) Some of the reactive free chlorine in the upper atmosphere is sequestered by reaction with methane according to this gas-phase reaction:

$$Cl + CH_4 \rightarrow CH_3 + HCl$$

Assuming that this reaction occurs in one bimolecular step, please **write a rate law for the process**.

rate = k [Cl][CH_4]

k) The overall equation for the production of gaseous ozone from stratospheric oxygen gas is:

$$3\ O_2 \rightarrow 2\ O_3$$

If this reaction is replicated under experimental conditions where the rate of consumption of molecular oxygen is 4.5 M/min, what would you expect to be the **rate of ozone production**?

$$\frac{4.5 \text{ moles } O_2}{L \cdot \text{min}} \times \frac{2 \text{ moles } O_3}{3 \text{ moles } O_2} = 3.0 \text{ moles } O_3 / L \cdot \text{min} = 3.0 \text{ M/min}$$

l) According to the collision theory of reactions **why does temperature affect the rate** of a chemical reaction? Please explain briefly. If you discuss more than one factor, be sure to indicate which factor is the most important. (3 points)

Increasing temperature increases the kinetic energy of particles. Increasing kinetic energy of particles increases both the frequency and the energy of the collisions between particles. The increased energy of collisions is the important thing, for it increases the probability that each collision will have sufficient energy to overcome the activation barrier and result in a productive chemical change.

m) In lab this week, you observed that both yeast cells and potassium iodide crystals can increase the rate of decomposition of hydrogen peroxide because both contain catalysts for this reaction. What is the fundamental means by which catalysts affect the rate of chemical reactions?
(3 points)

Catalysts increase reaction rates by decreasing the activation energy required for productive reaction.

n) Consider three containers, each filled with carbon dioxide gas and liquid water. The amount of CO_2 and H_2O is the same for all three containers. Container #1 is at 25 ºC and 1 atm pressure, container #2 is at 50 ºC and 1 atm pressure, and container #3 is at 25 ºC and 5 atm pressure. **Relative to container #1, will container #2, #3, neither, or both have a higher concentration of carbon dioxide dissolved in the water?**

An increase in Pressure will cause more gas molecules to collide with the surface of the water and thus to become dissolved in the water. So **#3** will have a higher concentration of dissolved CO_2. An increase in temperature (#2) will DEcrease the solubility of a gas in a liquid.

2. **Structure and intermolecular interactions.**

a) Would you expect hexane ($CH_3CH_2CH_2CH_2CH_2CH_3$) or butanol ($CH_3CH_2CH_2CH_2OH$) to be more soluble in ligroine (also known as petroleum ether, the solvent that you used to extract fat from your food samples in lab two)? Please explain your answer carefully, making specific reference to the structures of these molecules. (4 points)

Ligroin was used for the extraction of fat because it is a non-polar solvent.
Hence the more non-polar of these two molecules, hexane, will dissolve more effectively in it.
Another way to look at this is to ask which of these two molecules will be able to form more effective intermolecular interactions with the solvent. The solvent is only capable of forming dispersion interactions, so the strength of dispersion interactions will determine the better solute; hexane has a higher molar mass, and more electrons, so it will be more polarizable and will form stronger dispersion interactions.
By both criteria, Hexane is predicted to be more soluble.

b) In lab two, you used extraction and filtration to separate your fat from other kinds of molecules in your food samples. Another common technique for separating molecules based on their properties is *chromatography*. In Chem 121, you created a chromatography column from Tide detergent granules, and used it to distinguish between molecules carried on a mobile phase of natural gas. A common set-up for liquid chromatography experiments consists of an aqueous mobile phase and a stationary phase composed of C_8H_{17} "tails" attached to small solid beads and packed into a glass cylinder. (For any gear-heads out there, this is called C8-Reverse Phase Liquid Chromatography.)

Suppose that three compounds -- CH_3OH, C_3H_7OH, and C_3H_7Cl -- were loaded into one end of the cylinder and then the mobile phase was allowed to flow through the column. **In what order would you expect these compounds to pass through the column?** (i.e., which would spend the least time interacting with the column? which would spend the most time?) Please explain your answer carefully, showing why each of these compounds would travel at the relative rate that you are predicting, given this column and this mobile phase. (5 points)

The column is C_8H_{17} -- it is non-polar, and can only interact with other molecules via dispersion forces
The mobile phase is water -- it is polar, and can interact with analyte molecules via dipole-dipole and hydrogen bonding as well as dispersion forces.

CH_3OH -- the lightest of the analyte molecules, and thus capable of the weakest dispersion interactions; can form H-bonds
C_3H_7OH -- midway in mass and therefore midway in magnitude of dispersion forces
C_3H_7Cl -- the heaviest and therefore capable of the strongest interactions with the column; incapable of forming hydrogen bonds

The analyte most likely to interact with the mobile phase is methanol; it is also least likely to interact with the column, and so it will wash off the column quickly.
The analyte least inclined to interact with the mobile phase is C_3H_7Cl; it is also most likely to interact with the column, and so it will stay on the column the longest.
The propanol falls in between.

3. **Light and bonds.**

a) Please use the following MO diagrams to illustrate which of the following two molecules should have the **greater bond length**: Carbon monoxide or nitrogen monoxide. Be sure to explain your conclusion. (3 points)

Carbon monoxide (10 valence electrons)

σ_{2p}^* —

π_{2p}^* — —

σ_{2p} _||_

π_{2p} _||_ _||_

σ_{2s}^* _||_

σ_{2s} _||_

Bond order = ½ (8-2) = 3

Nitrogen monoxide (11 valence electrons)

σ_{2p}^* —

π_{2p}^* _|_ —

σ_{2p} _||_

π_{2p} _||_ _||_

σ_{2s}^* _||_

σ_{2s} _||_

Bond order = ½ (8-3) = 2.5

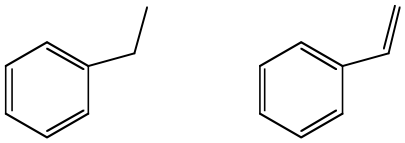
The bond in carbon monoxide is of higher order, so it is stronger and shorter than the bond in nitrogen monoxide. Nitrogen monoxide has the longer bond.

b) In lab last week, you measured the absorbance of light by Koolaid solutions containing the food dye Allura Red (also known as Red Dye #40). In the class session before the lab, I mentioned that the energy difference between the HOMO and the LUMO for this dye is 57 kcal/mol. Please predict the **wavelength** (in nm) **of maximal absorbance** (λ_{max})that should be observed for this molecule. Be sure to show all your calculations. (3 points)

57 kcal is enough energy to excite one mole of Red Dye #40. Converting to Joules and dividing by Avogadro's number shows that 3.96×10^{-19} Joules are required per molecule. This is the energy needed per photon of light.

$E = hc/\lambda \quad \lambda = hc/E = (6.63 \times 10^{-34})(3 \times 10^{8}) / (3.96 \times 10^{-19}) = 5.02 \times 10^{-7}$ m $= 502$ nm

c) Which of the following two molecules would you expect to **absorb light at a longer wavelength**? Please explain your answer briefly but carefully. (3 points)



The molecule on the right absorbs light of longer wavelength (248 nm) than the molecule on the left (208 nm). This is due to the higher level of conjugation in the right-hand molecule. Higher conjugation leads to greater electron delocalization, which correlates with reduced energy difference between MOs. Thus the molecule with higher conjugation should have a smaller HOMO-LUMO energy gap, and its HOMO electrons will be excited by lower energy light -- light with a longer wavelength.